

Reductive Dechlorination of Trichloroethene Mediated by Humic–Metal Complexes

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Experiments were conducted to determine if transition metal–humic acid complexes can act as e^- transfer mediators in the reductive dechlorination of trichloroethene (TCE) using Ti(III) citrate as the bulk reductant. In the presence of Ni–Aldrich humic acid (AHA) complexes, TCE reduction was rapid, with complete removal of TCE in less than 23 h. Cu–AHA complexes were less effective as e^- mediators than Ni–AHA complexes; only 60% of TCE was reduced after 150 h. Partially dechlorinated intermediates were observed during TCE reduction; however, they were transitory, and at no time accounted for more than 2% of the initial TCE mass on a mole C basis. Ethane and ethene were the primary end products of TCE reduction; however, a suite of other non-chlorinated hydrocarbons consisting of methane and C₃ to C₆ alkanes and alkenes were also observed. The results suggest that humic–metal complexes may represent a previously unrecognized class of electron mediators in natural environments.

Introduction

Chlorinated ethenes (CE) are a class of chlorinated solvents (CS) which have been used extensively in a range of commercial and industrial applications. Prior to the adoption of current regulatory protocols, commonly accepted handling and disposal practices have resulted in extensive groundwater contamination. As a class, CEs have been of particular concern because in several cases both the parent compound and partially dechlorinated transformation products pose environmental and human health hazards. Extensive research into the environmental fate of these compounds over the past several decades has shown that they can be transformed by both biotic and abiotic processes through substitution, dehydrohalogenation, and oxidation and reduction reactions. CSs released into aquatic and terrestrial environments commonly encounter reducing conditions (e.g. anoxic soils, sediments, and groundwaters). Anoxic environments are often sufficiently reducing to make reductive dechlorination reactions thermodynamically favorable. However, the transfer of electrons from the reductant to the given CS is often kinetically constrained, thus resulting in relatively slow transformation rates *in situ*. The reduction rate may be enhanced by the addition of a compound capable of facilitating the transfer of electrons from the bulk reductant to the CS of interest. A number of compounds have been

shown to be capable of acting as e^- transfer mediators for the reductive dechlorination of CS using several different bulk reductants. Several transition metal organocomplexes including vitamin B₁₂ (Co), hematin (Fe) and related iron porphyrins, and coenzyme F₄₃₀ (Ni) have proven to be effective e^- transfer mediators in the reductive dechlorination of carbon tetrachloride (CT), hexachloroethane (HCE), and several chlorinated ethenes including trichloroethene (TCE) using Ti(III) citrate or reduced organic sulfur compounds as bulk reductants (1–9). In addition, several low molecular weight quinones, dissolved organic carbon (DOC), and humic substances have been shown to be effective e^- mediators in the reduction CT and HCE by hydrogen sulfide or Fe(II)_{aq} (9–11). The presence of quinone moieties within the structure of DOC and humic substances has been suggested to explain their ability to act as e^- mediators in reduction reactions (10, 12).

Humic substances (HS) are a class of naturally occurring, biogenic, refractory organic oligoelectrolytes which are present in both aquatic and terrestrial environments (13). HS have been shown to complex a wide range of transition metals (14–16). The purpose of this research was to determine if humic–metal complexes can act as e^- mediators in the reductive dechlorination of TCE, the most common CS contaminant found in subsurface environments.

Experimental Section

Experiments were carried out in 160 mL serum bottles sealed with aluminum crimp caps and Teflon-lined rubber septa. Each bottle contained 100 mL of solution phase and 60 mL headspace. Aldrich humic acid (AHA) was treated extensively to remove residual fulvic acids and inorganic impurities including metals (17). Briefly, AHA was dissolved in 10^{−2} M NaOH followed by treatment with HF–HCl and Na saturated with Na–Chelex 100 (Bio-Rad Laboratories, Hercules, CA). Excess sodium was removed by dialyzing against Milli Q water using 1000 MWCO cellulose ester dialysis tubing. Ti(III) citrate was prepared as described by Smith and Woods (18).

Experimental systems were prepared by adding 90 mL of either deoxygenated (Ar-sparged for >1 h) 11.1 mg OC L^{−1} AHA or deoxygenated Milli-Q water to each bottle followed by 1.0 mL 10^{−2} M M in 0.1 M HCl (where M is either Co(II), Cr(III), Cu(II), Fe(II), Mn(II), Mo(VI), Ni(II), V(IV), or Zn(II); these transition metals were chosen based on their relative natural abundance and/or their demonstrated role in biochemical redox reactions) and 0.1 mL 1 M NaOH. After 24 h 6 mL of 250 mM Ti(III) citrate and 3 mL of 2 M Tris buffer (pH 7.8) were added and the bottles were sealed. The E_h of the systems containing Ti(III) citrate was −700 mV as measured with a platinum redox electrode. Reactions were initiated by the addition of 2 μ L of TCE/*n*-heptane solution (1.0 g/0.2 g); *n*-heptane was added as an internal standard. Experimental systems were prepared in duplicate. Initial solution concentrations were 10 mg OC L^{−1} AHA, 100 μ M M, 100 mM Tris, and 15 mM Ti(III) citrate; the total mass of TCE in each vial was 16.0 μ mol, with 80% partitioned in the aqueous phase. The presence of 10 mg OC L^{−1} AHA had no measurable effect on TCE water-vapor partitioning. The bottles were placed on a roller drum and rotated vertically as the bottle axis remained horizontal and maintained at 20 °C in the dark. All preparative work was performed in an anaerobic glovebox with an atmosphere of 4–6% H₂, bal N₂ (the amount of H₂ had no observable effect on the rate or extent of reaction) or under continuous argon sparging.

At selected intervals, 100 μ L headspace samples were removed from the reaction bottles for analysis using a

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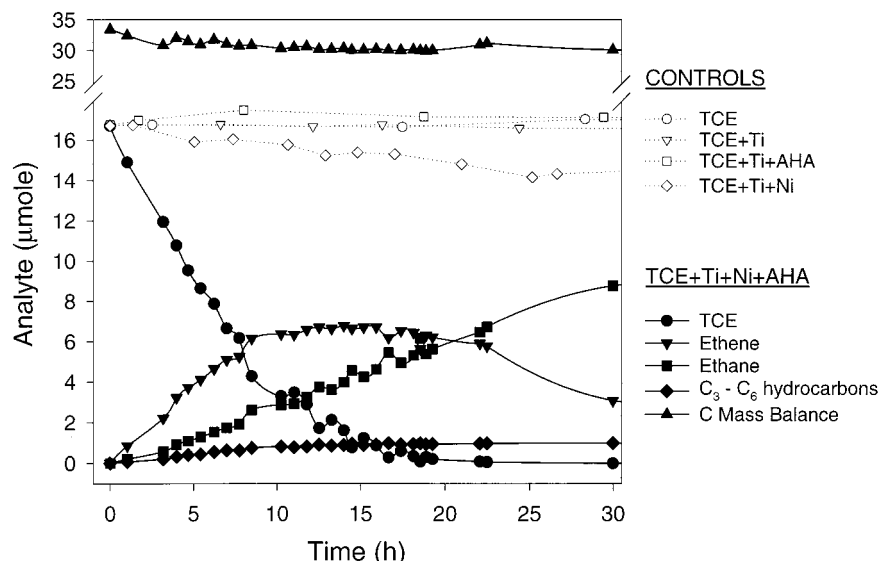


FIGURE 1. Ni–Aldrich HA mediated reduction of TCE in solution containing 10 mg OC L⁻¹ AHA, 100 μ M Ni²⁺, 100 mM Tris, and 15 mM Ti(III) citrate as the bulk reductant in batch systems (100 mL aqueous phase; 60 mL vapor phase) at 20 °C. Carbon mass balance pertains to TCE and identified TCE reduction products only. (Plots are of data from duplicate vials.)

Hewlett-Packard 5890 Series II gas chromatograph with a GSQ column (0.53 mm by 30 m) and a flame ionization detector (240 °C). The oven temperature program was 50 °C for 2 min, ramp 25 °C min⁻¹ to 200 °C, and hold for 12 min. The system was calibrated by equilibrating known masses of analytes and internal standard (*n*-heptane) in serum vials containing the same ratio of aqueous phase to vapor phase as the experimental systems, thus accounting for water-vapor partitioning and allowing analyte concentrations to be expressed on a mass per bottle basis. Vapor/liquid exchange in these systems was rapid (90% of equilibrium is reached within 5 min) relative to the reaction kinetics. The identities of reaction products and intermediates were confirmed by GC/MS using a Hewlett-Packard 5890 Series II gas chromatograph with a model 5971 mass selective detector. The oven temperature program was 40 °C for 3 min, ramp 25 °C min⁻¹ to 200 °C, and hold for 14 min. Detector temperature was 280 °C.

Results and Discussion

Of the nine transition metal–humic complexes examined, only Ni– and Cu–AHA complexes demonstrated any activity as *e*⁻ transfer mediators in the reductive dechlorination of TCE with Ti(III) citrate as the bulk reductant. Reduction of TCE was rapid in the presence of Ni–AHA; complete removal was observed within 23 h (Figure 1). Over the same time period < 14% of the TCE was reduced in the system containing Ni without AHA. While Ti(III) citrate is a strong reductant, in the absence of an effective *e*⁻ mediator, it is essentially nonreactive with respect to the reductive dechlorination of TCE over the time scale of these experiments. Though dissolved organic carbon (DOC) and humic materials have been shown to be effective *e*⁻ mediators in the reduction of nitroaromatic compounds, HCE, and CT (10, 12), AHA alone (i.e. without the addition of Ni) was not an effective *e*⁻ mediator for the reduction of TCE by Ti(III) citrate (see Figure 1). The reductive dechlorination of TCE has been well studied (e.g. ref 19) and has been shown to proceed via a number of mechanisms involving a suite of potential intermediates (Figure 2). In the presence of Ni–AHA, TCE was rapidly reduced to ethene, which was further reduced to ethane (Figure 1). The presence of *cis*- and *trans*-1,2-dichloroethene, 1,1-dichloroethene, vinyl chloride, chloroacetylene, and acetylene was confirmed by GC-MS; however, these products were transitory and at no time accounted for more than 2% of the initial TCE mass on a mole C basis. In contrast to

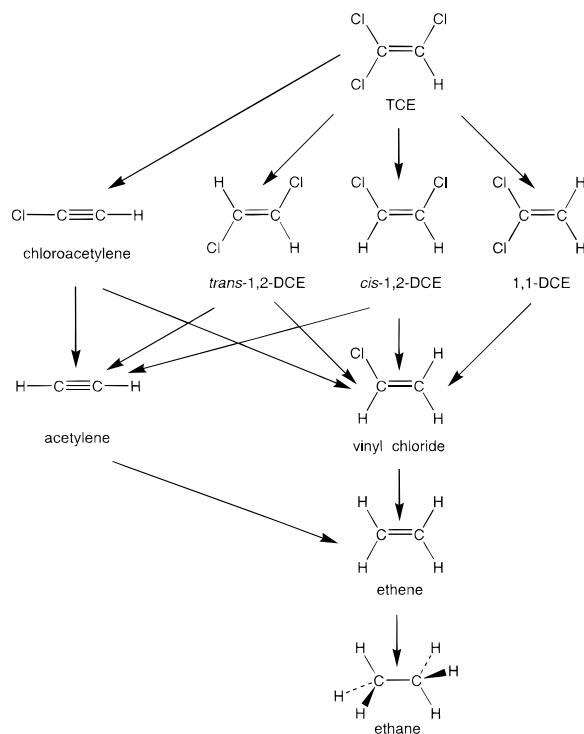


FIGURE 2. Potential pathways, intermediates, and end products of TCE reductive dechlorination.

vitamin B₁₂ mediated TCE reduction, where *cis*-1,2-dichloroethene is the major end product (1, 2, 5), ethane and ethene were the major products of Ni–AHA mediated TCE dechlorination, accounting for over 70% of TCE derived C. A suite of other non-chlorinated hydrocarbons consisting of methane and C₃ to C₆ alkanes and alkenes were also observed. The non-C₂ hydrocarbons, with the exception of methane, are likely the result of radical coupling reactions. These hydrocarbon products were not observed in controls containing Ti(III) citrate, Ni²⁺, *n*-heptane, and AHA but without the addition of TCE, indicating that they are derived from the products of TCE reduction (data not shown). The production of methane and C₃ to C₅ alkanes and alkenes has also been observed during the reduction of TCE by zerovalent iron, and experiments using ¹³C₂-labeled TCE indicate that they are derived predominantly from products of TCE reduction

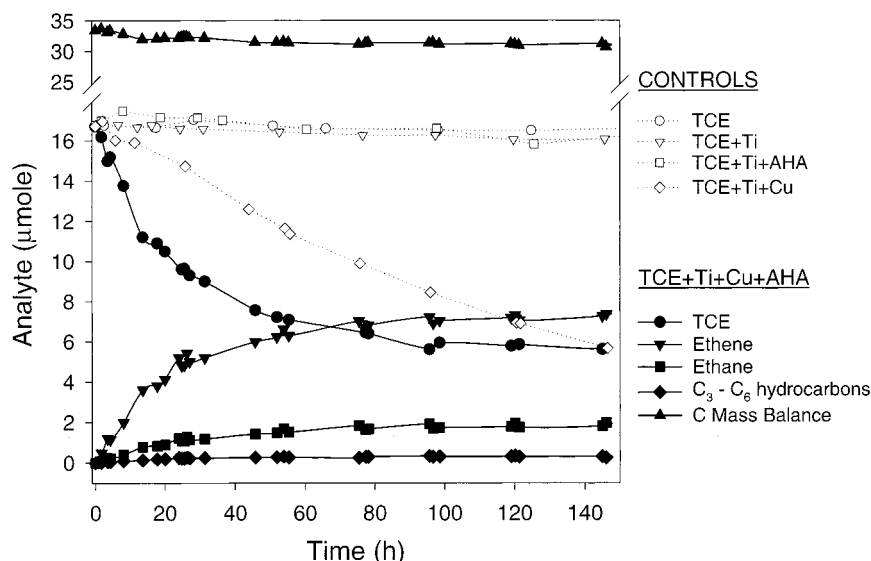


FIGURE 3. Cu–Aldrich HA mediated reduction of TCE in solution containing 10 mg OC L⁻¹ AHA, 100 μM Cu²⁺, 100 mM Tris, and 15 mM Ti(III) citrate as the bulk reductant in batch systems (100 mL aqueous phase; 60 mL vapor phase) at 20 °C. Carbon mass balance pertains to TCE and identified TCE reduction products only. (Plots are of data from duplicate vials).

(20). In total, the hydrocarbon products accounted for approximately 90% of TCE derived C; the unrecovered C suggests the possibility of unidentified products.

Cu–AHA complexes were less effective as mediators than Ni–AHA complexes; the total mass of TCE in the system dropped to ~6 μmol after 95 h and remained relatively unchanged thereafter (Figure 3). Though the transformation of TCE was slower in the system containing Cu without AHA, after 150 h the extent of reaction was the same as the Cu–AHA system. Transformation of TCE in the controls containing Ti(III) citrate and Ti(III) citrate with AHA was minimal (<5%). The major products of TCE reduction were the same as in the Ni–AHA system; however, there was substantially less reduction of ethene to ethane. Similarly, methane and C₃ to C₆ alkanes and alkenes were also observed. Final C mass recovery was approximately 93%, again suggesting possible unidentified products.

In controls containing Cu (and to a much lesser extent Ni) but without AHA, TCE reduction in excess of the Ti(III) citrate control was observed. These results suggest that the hydrated metal ion or other metal complex species may also act as e⁻ mediators. Though AHA was not added to these systems, the solution phase contains Tris buffer and citrate, both of which form complexes with Cu and Ni (21, 22); these complexes may have the capacity to act as e⁻ mediators for the reductive dechlorination of TCE.

The data presented suggest that humic metal complexes may represent a previously unrecognized class of e⁻ mediators in natural environments. Research is currently underway to determine the extent to which Ni and Cu complexes of humic substances isolated from soils and natural waters can act as e⁻ mediators for the reductive dechlorination of TCE, to characterize the mechanism(s) involved in these reactions, to determine the extent to which humic–metal complexes can mediate reduction reactions with other compounds of environmental concern, and to determine the ability of environmentally relevant bulk reductants to drive these reactions.

Acknowledgments

Financial support for this project was provided, in part, by the Air Force Office of Scientific Research and is gratefully acknowledged.

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Received for review September 28, 1998. Revised manuscript received January 20, 1999. Accepted January 25, 1999.

ES9810033